*J. Sci. Food Agric.* 1986, **37**, 632–636

# Chemical Composition and In-vitro Digestibility of Thermochemically Treated Peanut Hulls

Thomas J. Kerr, William R. Windham[a], Janet H. Woodward and Ronald Benner

*Department of Microbiology, University of Georgia, Athens, Georgia 30602 and [a]Richard B. Russell Agricultural Research Center, USDA, ARS, Athens, Georgia 30613, USA*

*(Manuscript received 4 July 1985)*

Changes in chemical composition and digestibility of peanut hulls after a variety of thermochemical treatments were monitored. Mineral acids and base under elevated temperature (121°C) were generally ineffective for decreasing the fibrous, lignocellulosic component of the hulls. Only nitric acid-treatment effectively decreased the relative lignin content of the hulls. The lignin:nitrogen ratio and carbohydrate content of treated hulls were both highly correlated with in-vitro digestibility. Overall, thermochemical treatments did not increase the digestibility of peanut hulls.

*Keywords:* Peanut hulls; lignocellulose; in-vitro digestibility; fibre; thermochemical.

## 1. Introduction

Of the hundreds of thousands of tons of peanuts produced each year, a quarter of this production are the hulls. The majority of peanut hulls are burned in the open field, dumped in forest areas or blown into huge piles and left to naturally deteriorate. During the past few years various methods have been proposed to make use of peanut hulls, including, but not limited to, use as supplements to cattle feed,[1–4] carrier of insecticide,[5] manufacture of logs,[6] production of pulp[7,8] and even as a fibre additive to the human diet.[9] No one particular method, nor even all the methods combined, would use the tonnage of hulls produced each year. Even if the various methods mentioned above could use the total amount of peanut hulls, the limiting factor would not be the economics of use, but the high cost of transportation based on the volume:weight ratio. Unmilled peanut hulls weigh 80.2–115.5 kg $m^{-3}$; milled hulls, 6.35 mm in size, weigh 401–481 kg $m^{-3}$. Therefore, a method of using or processing the hulls at the shelling plant would be more economical. In addition, many of the suggested methods of utilisation would use only a portion of the hulls, thus leaving a waste product for which a means of disposal must be found.

One of the most interesting and practical methods suggested to date for the use of the peanut hull has been to increase the ruminant digestibility by chemical treatment and thus make them more nutritious as a cattle feed instead of merely roughage. Although peanut hulls contain between 6—7% crude protein, they also are composed of 60–67% crude fibre[5] which is believed to be one of the reasons that they are less than 20% digestible by ruminants. Barton *et al.*[1] attempted to increase the digestibility of peanut hulls by treating them with a variety of chemicals, including a number of delignifiers. The best results were obtained with a 1.82 M calcium hypochlorite treatment (100°C) which increased the in-vitro dry matter digestibility (IVDMD) of the hulls from 25% to 40%. Although this was a 60% increase in digestibility of the peanut hulls, it still did not compare favourably with the digestibility of soya bean hulls, or coastal bermuda grass, which have an IVDMD of 69.6% and 59.0%, respectively, without chemical treatment. Barton *et al.*[1] did not report any specific change in chemical composition of the hulls after treatment with the various chemicals, and the data indicated that all the treatments to which the hulls were subjected, except the calcium hypochlorite treatment, actually decreased the digestibility of the peanut hulls. Why this decrease in digestibility occurred when the peanut hulls were subjected to delignification procedures remains unexplained. It was stated that the cellulose fraction of peanut hulls was less digestible than the cellulose fractions of certain grasses and that this difference could be caused by (a) degree of polymerisation, (b) crystallinity, (c) branching, (d) sites and number of cross linkage with other plant polymers, or a combination of these four conditions.

Although a number of papers have been published which give a chemical analysis of raw peanut hulls or describe the chemical composition of specific components of the hull,[1, 9–17] there are no publications that detail the compositional change as the result of various chemical treatments. Likewise, there are several publications that report changes in digestibility of hulls or their degree of saccharification when subjected to different mechanical, chemical, and enzymic treatments,[1, 4] but none that compare the change in chemical composition and digestibility.

In this study changes are reported in percentages of different chemical components of peanut hulls after they have been subjected to various thermochemical treatments. An attempt is also made to determine a correlation between the chemical composition of the hulls and the degree of in-vitro digestibility.

## 2. Experimental

Peanut hulls were obtained from the Columbian Peanut Co, Ozark, AL and the Damascus Peanut Co, Damascus, GA. Hulls were supplied whole (as they come from the shelling machine) and hammer-milled to either 3 or 6 mm. Hulls were obtained from the Florunner variety of peanut (*Arachis hypogeae*). All the chemicals used were of reagent grade and were obtained from Sigma Chemical Co, St. Louis, MO or Fisher Scientific Co, Atlanta, GA.

### 2.1. Chemical treatment

Before any chemical treatment, 5 samples of the peanut hulls were dried at 70°C for 24 h to determine the weight of undried hulls required to provide 100 g of dry weight hulls. An equivalent of 100 g of oven dried, 6 mm hammer-milled peanut hulls, was treated with 1 litre of each of the following: distilled water, ethanol (95%), hydrochloric acid (0.5 M), sulphuric acid (0.25 M), nitric acid (0.5 M), acetic acid (0.5 M), sodium hydroxide or ammonium hydroxide (0.5 M). Treatment was carried out for 1 h at 121°C. The solutions were cooled to room temperature, filtered and the hulls treated with acid or alkali were washed with tap water until the rinse water was of neutral pH. Hulls were oven dried at 70°C for 24 h and weighed. Triplicate samples were used for all procedures.

### 2.2. Chemical analysis

Moisture content of the peanut hulls was determined by weighing 100 g samples before and after placing them in a drying oven at 70°C for 24 h. Samples to be used in other analyses were placed in a desiccator until needed. Five samples were allowed to remain outside the desiccator for 7 days, and were weighed to determine the amount of moisture absorbed from the atmosphere.

Nitrogen determinations were made on oven dried samples using the Kjeldahl procedure.[18] Protein was calculated as N×6.25. Carbohydrates were extracted from the hulls using boiling 70% ethanol. One gram of hulls was treated with 100 ml of 70% ethanol for 1 h. The material was boiled in a beaker with a cover glass top to avoid liquid loss. The liquid was cooled, filtered and evaporated to dryness, then reconstituted to 100 ml with distilled water. The extracted hulls were oven dried at 70°C for 24 h and weighed. Total carbohydrates were determined using the procedure of Morris.[19] Cellulose was determined by the procedure of Updegraff.[20] Acid insoluble lignin was determined by the method described by Van Soest.[21] All samples were analysed in triplicate; arithmetical means are presented in Table 1. The Tilley–Terry[22] procedure was used to determine the in-vitro digestibility of each sample. Three separate runs of chemically

**Table 1.** Chemical composition and digestibility (IVDMD) of thermochemically treated peanut hulls

| Treatment | Protein (%) | Lignin (%) | Cellulose (%) | Carbohydrate (%) | Digestibility (%) |
|---|---|---|---|---|---|
| Control | 8.2 | 28.8 | 37.0 | 2.5 | 26.0 |
| Hydrochloric acid (0.5 M) | 5.5 | 40.0 | 37.0 | 0.4 | 0.2 |
| Sulphuric acid (0.25 M) | 5.3 | 38.5 | 24.0 | 0.5 | 1.4 |
| Nitric acid (0.5 M) | 6.7 | 25.2 | 41.5 | 0.9 | 6.9 |
| Acetic acid (0.5 M) | 7.7 | 31.5 | 32.0 | <0.1 | 4.9 |
| Sodium hydroxide (0.5 M) | 6.9 | 35.3 | 29.5 | 1.5 | 9.9 |
| Ammonium hydroxide (0.5 M) | 6.4 | 35.3 | 45.0 | 0.5 | 5.0 |
| Water | 8.8 | 32.8 | 40.5 | 0.8 | 7.8 |
| 95% Ethanol | 9.1 | 33.8 | 27.0 | 1.6 | 14.5 |

treated and untreated hulls were analysed in duplicate for IVDMD. Arithmetical means of these analyses are presented in Table 1.

## 3. Results

The weight loss of peanut hulls treated with the various chemicals ranged from 4.8 to 38.7%, with acetic acid causing the least weight loss and nitric acid causing the greatest weight loss (Table 2). After each chemical treatment, the remaining material was analysed for protein, lignin, cellulose, and total carbohydrate content.

The relative percentage of protein remaining in the hulls after chemical treatment varied from a high value of 9.1% for hulls treated with 95% ethanol to a low value of 5.3% for hulls treated with sulphuric acid (Table 1). Hulls treated with either acid or alkali lost a significant amount of protein while hulls treated with water or ethanol increased in the relative percentage of protein. Carbohydrate content of the hulls decreased after each of the various chemical treatments (Table 1). Acetic acid removed over 95% of the carbohydrates. The relative percentage of cellulose increased in the hulls treated with nitric acid, ammonium hydroxide, or water, but decreased when hulls were treated with sulphuric acid, acetic acid, or sodium hydroxide (Table 1). The relative percentage of cellulose in hulls treated with hydrochloric acid was the same as in raw peanut hulls. Of all the treatments, only nitric acid was found to be an efficient delignifier. The relative percentage of lignin increased in hulls treated by all of the chemicals except nitric acid which caused a 3.6% decrease in the relative percentage of lignin (Table 1).

All thermochemical treatments of the peanut hulls decreased digestibility in rumen liquor significantly. The most drastic reduction in digestibility occurred in hulls treated with hydrochloric acid, which had a digestibility of less than 1% (Table 1). Treatment of hulls with ethanol decreased digestibility by 46% relative to raw peanut hulls. Of all the chemical treatments, ethanol-treated hulls were the most digestible (Table 1).

**Table 2.** Weight loss from 6 mm hammer-milled peanut hulls after thermochemical treatments

| Treatment[a] | Initial weight[b] (g) | Final weight[c] | Weight loss (%) |
|---|---|---|---|
| Hydrochloric acid (0.5 M) | 100 | 68.8 | 31.2 |
| Sulphuric acid (0.25 M) | 100 | 77.7 | 28.3 |
| Nitric acid (0.5 M) | 100 | 61.3 | 38.7 |
| Acetic acid (0.5 M) | 100 | 96.0 | 4.0 |
| Sodium hydroxide (0.5 M) | 100 | 89.6 | 10.4 |
| Ammonium hydroxide (0.5 M) | 100 | 86.3 | 13.7 |
| Water | 100 | 92.8 | 7.2 |
| 95% Ethanol | 100 | 81.4 | 18.2 |

[a] One litre liquid for 1 h at 121°C.

[b] Raw peanut hulls equivalent to 100 g of oven dried hulls. Average moisture content of peanut hulls was 12.1%, $n=5$.

[c] Dry weight determined after hulls were dried for 24 h at 70°C.

## 4. Discussion

Many attempts have been made to correlate digestibility of lignocellulosic materials with a variety of parameters such as total fibre content, lignin content, and total nitrogen content.[23–26] From these studies it can be generalised that fibre and lignin content are negatively correlated with digestibility; whereas, nitrogen content is positively correlated with digestibility. It is hoped that by monitoring changes in chemical composition of peanut hulls after various thermochemical treatments, changes in digestibility can be predicted.

Treatment of lignocellulosic material with various chemicals, such as sodium hydroxide, under elevated temperature and pressure is known to destroy the integrity of many inter- and intrapolymeric linkages.[23] Such treatment is the basis of the pulping industry for delignifying woody material. However, the sodium hydroxide treatments used in this study failed to remove the lignin component of peanut hulls. Instead, only treatment with nitric acid resulted in a decrease in lignin content of the hulls. Thus, on the basis of lignin content alone, it would be predicted that nitric acid-treated hulls would be more digestible than sodium hydroxide-treated hulls. On the contrary, nitric acid-treated hulls were found to be less digestible than sodium hydroxide-treated hulls. However, neither treatment increased the digestibility of hulls; lignin content of hulls after the various treatments correlated negatively ($r=-0.529$) with digestibility.

No correlation was found between cellulose content and digestibility of the hulls ($r=0.004$); whereas the protein or nitrogen content of hulls was positively correlated ($r=0.663$) with digestibility. However, the lignin:nitrogen ratio of chemically treated hulls was a better indicator of digestibility ($r=-0.716$; $P<0.05$). Lignin:nitrogen ratios have been used to predict the biodegradability of plant litter,[27,28] and may be useful for predicting the ruminant digestibility of lignocellulosic materials. Nitrogen content indicates the amount of highly digestible cellular contents present in the material, whereas, lignin content indicates the amount of cell wall material, which is relatively indigestible.[25] Therefore, lignin:nitrogen ratios of lignocellulosic materials can better predict the overall digestibility of the plant material than nitrogen or lignin content alone. Neither the lignin:cellulose ratio ($r=-0.401$) nor the lignin:carbohydrate ratio ($r=-0.419$) predicted the digestibility of the hulls as well as the lignin:nitrogen ratio.

The chemical component of peanut hulls most highly correlated ($r=0.931$; $P<0.001$) with digestibility was the total carbohydrate content. All of the treatments removed carbohydrates and all treatments reduced digestibility. Hulls treated with sodium hydroxide had more carbohydrate than hulls treated with nitric acid and this may be the reason why sodium hydroxide-treated hulls were more digestible than nitric acid-treated hulls, even though nitric acid treatment removed a significant portion of lignin from the hulls. However, the difference in carbohydrate content (0.6%) between nitric acid-treated and sodium hydroxide-treated hulls is not sufficient to account for the 3% higher digestibility of sodium hydroxide-treated hulls. Thus, carbohydrate content is an indicator of some other factor also involved in the digestibility of peanut hulls.

Digestibility of peanut hulls is very low and none of the treatments demonstrated here increased the digestibility of hulls. It was surprising that the treatment of peanut hulls with sodium hydroxide failed to increase digestibility. Treatment with alkali has been successful in increasing the digestibility of many other agricultural waste products.[29–33] Dekker and Richards[34] reported a 2.7-fold increase in digestibility of bagasse after a three hour treatment with 7% NaOH, and this correlated with a 16% decrease in crude lignin content (27.5% to 11.5%). Based on this information it was stated that the results confirm that digestibility is increased as lignin is removed. While there does appear to be some correlation between lignin content of peanut hulls and digestibility, the results presented here and those of Barton *et al.*[1] suggest that other factors are also involved in the resistance of hulls to decomposition in rumen liquor.

## References

1. Barton, F. E.; Amos, H. E.; Albrecht, W. J.; Burdick, D. Treating peanut hulls to improve digestibility for ruminants. *J. Animal Sci.* 1974, **38,** 860–864.

2. Burdick, D.; Barton, F. E.; Amos, H. E. Performances of steers fed peanut hulls as roughage, weight gain and DDT residues. *US Agric. Res. Service report* 1975, ARS-S-61, 9.
3. Lutz, J. A.; Jones, G. D. Effect of peanut hulls on the performance of corn. *Agron. J.* 1978, **70,** 784–786.
4. Utley, P. R.; McCormick, W. C. Level of peanut hulls as a roughage source in beef cattle finishing diets. *J. Anim. Sci.* 1972, **34,** 145–151.
5. Albrecht, W. J. Peanut hulls: Their properties and potential uses. *USDA Report* ARM-S-1/January 1979.
6. Albrecht, W. J.; Barton, F. E.; Burdick, D. Peanut hulls for manufacturing artificial fireplace logs. *Trans. ASAE* 1973, **16,** 650–652.
7. Glasser, W. G.; Slupski, R. H.; Clark, J. P. Pulp and paper making potential of peanut hull waste in blends with softwood pulp. *Wood and Fiber* 1973, **5,** 98–100.
8. Govil, R. S. Chemical pulp from groundnut shell. *TAPPI* 1960, **13,** 215–216.
9. Childs, S.; Bajian, A. A. Physico-chemical characterization of peanut hull as potential fiber additive. *J. Food Sci.* 1976, **41,** 1235–1236.
10. Brennan, J. R. The peanut gynophere. *Biologist* 1969, **51,** 71–72.
11. Fraps, G. S. The composition of peanuts and peanut by-products. *Texas Agric. Exp. Sta. Bull.* 1917, **222,** 38.
12. Lynch, D. F. J.; Goss, M. J. Peanut hull cellulose. *Ind. Eng. Chem.* 1930, **22,** 903–906.
13. Morrison, F. B. *Feeds and Feeding* The Morrison Publishing Company, Ithaca, NY, 1956, 22nd edn, p. 1165.
14. Radhakrishnamurthy, B.; Srinivasan, V. R. Peanut shells. I. Proximate analysis and the sugar make-up of the hemicellulose fractions. *J. Sci. Ind. Res.* 1957a, **16C,** 59–61.
15. Radhakrishnamurthy, B.; Srinivasan, V. R. Peanut shells. II. Chemical constitution of peanut shell hemicellulose A. *Proc. Indian Acad. Sci.* 1957b, **46A,** 53–60.
16. Radhakrishnamurthy, B.; Srinivasan, V. R. Studies on peanut shells. III. Structure of groundnut shell hemicellulose B1. *Proc. Indian Acad. Sci.* 1959, **49A,** 98–103.
17. Radhakrishnamurthy, B.; Srinivasan, V. R. Studies on groundnut shells. IV. Structure features of hemicellulose $B_2$, $C_1$, and $C_2$. *J. Sci. and Industr. Res.* 1960, **19C,** 157–158.
18. AOAC. Nitrogen-Micro-Kjeldahl Method—Official Final Action. In: *Official Methods of Analysis* Association of Official Analytical Chemists, Washington DC, 1975, 12th edn, pp. 927–928.
19. Morris, D. L. Quantitative determination of carbohydrates with Drywood's anthrone reagent. *Science* 1948, **107,** 254–255.
20. Updegraff, D. M. Semi-micro determination of cellulose in biological material. *Anal. Biol.* 1969, **32,** 420–424.
21. Van Soest, P. J. Use of detergents in the analysis of fibrous feeds. II. A rapid method for determination of fiber and lignin. *J. Ass. Offic. Agric. Chemist,* 1963, **46,** 829–835.
22. Tilley, J. M. A.; Terry, R. A. Two stage technique for the *in vitro* digestion of forage crops. *J. Brit. Grassl. Soc.* 1963, **18,** 104–111.
23. Fan, L. T.; Lee, Y-H.; Gharpuray, M. M. The nature of lignocellulosics and their pretreatments for enzymatic hydrolysis. *Adv. Biochem. Eng.* 1982, **23,** 157–187.
24. Kirk, T. K.; Moore, W. E. Removing lignin from wood with white-rot fungi and digestibility of resulting wood. *Wood and Fiber* 1972, **4,** 72–79.
25. Van Soest, P. J. Development of a comprehensive system of feed analyses and its application to forages. *J. Anim. Sci.* 1967, **26,** 119–128.
26. Van Soest, P. J.; Mertens, D. R.; Deinum, B. Preharvest factors influencing quality of conserved forage. *J. Anim. Sci.* 1978, **47,** 712–720.
27. Melillo, J. M.; Aber, J. D.; Muratore, J. F. Nitrogen and lignin control of hardwood leaf litter decomposition dynamics. *Ecology* 1982, **63,** 621–626.
28. Benner, R.; Moran, M. A.; Hodson, R. E. Effects of pH and plant source on lignocellulose biodegradation rates in two wetland ecosystems, the Okefenokee Swamp and a Georgia salt marsh. *Limnol. Oceanogr.* 1985, **30,** 489–499.
29. Chandra, S.; Jackson, M. G. A study of various chemical treatments to remove lignin from course roughages and increase their digestibility. *J. Agric. Sci. Camb.* 1971, **77,** 11–17.
30. Huffman, J. G.; Kitts, W. D.; Krishnamurti, C. R. The effects of alkali treatment and gamma irradiation on the chemical composition and *in vitro* rumen digestibility of certain species of wood. *Can. J. Anim. Sci.* 1971, **51,** 457–464.
31. Millett, M. A.; Baker, A. J.; Feist, W. C.; Mellenberger, R. W.; Slatter, L. D. Modifying wood to increase its *in vitro* digestibility. *J. Anim. Sci.* 1970, **31,** 781–788.
32. Singh, M.; Jackson, M. G. The effect of different levels of sodium hydroxide spray treatment of wheat straw on consumption and digestibility by cattle. *J. Agric. Sci. Camb.* 1971, **77,** 5–10.
33. Wilson, R. K.; Pigden, W. J. Effect of sodium hydroxide treatment on the utilization of wheat straw and poplar wood by rumen microorganisms. *Can. J. Anim. Sci.* 1963, **44,** 122–123.
34. Dekker, R. F. H.; Richards, G. N. Effect of delignification on the *in vitro* rumen digestion of polysaccharides of Bagasse. *J. Sci. Food Agric.* 1973, **24,** 375–379.